

SURFACE AREA MICROSTRUCTURE GAS DIFFUSION LAYER AND ITS EFFECTS ON MEA FUEL CELL

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Abstract

The Membrane Electrode Assembly (MEA) microstructure is the path in which the input gases, namely, hydrogen and compressed air, will follow through in the process of obtaining energy from the polymer electrode membrane fuel cell (PEMFC) system. The efficiency of the conversion is dependent on the microstructure model of the materials used in making this gas diffusion layer (GDL or gas diffusion electrode (GDE)). For every change in microstructure dimension, hence the electrical output obtained will be affected. Therefore, controlling the MEA microstructure in its fabrication is an imperative step in producing a good MEA. The controlling parameters used are the surface area of micro pore inside the Gas Diffusion Layer (GDL). The methods of BET are utilized in the study of surfaces, respectively; while the single stack fuel cell simulation is used in obtaining the current-voltage relationship. Results of the analyses showed that the current MEA Fuel Cell increasing as well as increasing surface area GDL. Whereas, surface area GDL is one of the parameter control to get GDL appropriate.

Keywords: surface area, cell potential fuel cell

1. INTRODUCTION

PEM Fuel Cell was electric power generator was used continuous way. It was as converter hydrogen into electric, whereas Hydrogen can be gotten from another natural resources such as air by using photovoltaic, plants as cane plant by cracking process and reforming process. At the first time, fuel cell was used for certain cases like electric generator and to produce water but for this time have been used transport power station and portable devices needs. Fuel Cell, using hydrogen gas and oxygen that theory for 1mol Hydrogen at atm, temperature 287°K, produce power of 237.200 Joule or equal 1.23 Volt electric. Although the air which was used Fuel Cell was not pure, humidification and hydrogen rate have been arranged so voltage maximum which was produced 1.16 volt at open circuit. Thus, Fuel Cell might not produce volt maximum of 1 mol Hydrogen (EG,2000). Besides that, in it application was needed volt about 200-300 volt installing cell in Fuel Cell stack was done in series manner. So that the stack was small enough thus fabrication of Fuel Cell stack used MEA cell. Base on mapping which was done in MEA fabrication, lowering of size and cost of PEM Fuel Cell fabrication was done by choice means process technique of MEA fabrication from Hot Pressing technique up to use Plasma technique. The focus of the main fabrication for decreasing thick and interest of catalyst Pt mg/cm² of MEA. For 'ink-based' interest catalyst about 0.15 mgPt/cm²-0.3 mgPt/cm² (Thomas,1998). This interest is the cost still high so the researches of engineering applied type of study method in micro scale manner. Then fabrication in micro scale manner have direct development until might get thick of MEA 300 micron into 15 nm (Spakovsky, 2000) and interest of catalyst Pt of MEA from 2 mgPt/cm² (Eisman, 1999) to 0.01 mgPt/cm² (Raimundo, 2002). In this study was using method which was well but done increasing of Fuel Cell performance by controlling of surface are of layers MEA structure at MEA Fuel Cell fabrication process

2. THEORY

Performance of fuel cell is dependent of surface area the mass transfer (EG, 2000) so surface area determined. According to Ruthven (1997) surface area material 200-1500 m²/g include type material microporous economic for MEA Fuel Cell (Sergei, 2002, Lean, 2002). In this paper, surface area material is determined base on diameter micropore while diameter pore determined by polymer compotition. Knowing

influence of surface area pore material in performance MEA fuel Cell, MEA consists five of layers like figure 1. Correlation surface area pore material toward performance MEA is explained as follows.

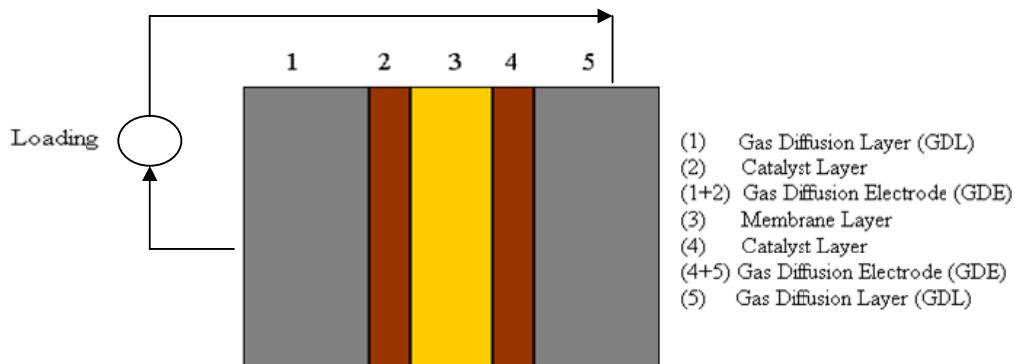


Fig 1. Membrane Electrode Assembly (MEA)

In MEA application, transport phenomena from gas H_2 and O_2 will occur in GDE. It will produce electron in layer and H_2O in layer (4). If in fabrication of size of GDE thick is small more compared of high, then gas flow in steady state at GDE and GDE producing heat perfectly so distribution modelling current electric is dependent gas diffusion, chemical reaction, ohmic loss (Marr,1997). Parameter determined current electric value that are surface area active, conductivity, gas diffusivity effective and reaction constanta in DGE layer. Evaluation in this is focussed in parameter of Diffusivity Effective of gas fluida in DGL, whereas the others parameter did not influence. If design GDL with diameter pore size close to diameter of molecul gas hydrogen and oksigen about 3.28 \AA (Xue-Dong , 1998, Ticianelli, 1988) but small more of 20 \AA Ruthven (1997) so each of pore diameter will be gotten surface area pore. If value of surface area pore GDL and gas diffusivity into parameter of performance MEA fuel Cell then will be gotten correlation between surface area with performance MEA fuel cell

3.EXPERIMENT

In experiment, process fabrication have two steps there are (1) formulation material by using design expert (2) coating Carbon Ink at karbon kloth by sprayer system. Sprayer system consists sprayer Gun and draying. The raw materials to grow material consists of Polymertetraflouroethylene, 60 w % dispersion in water (PTFE) (Aldrich chemical Co, Inc), activated carbon (Ajax chemicals), carbon cloth (E-TEK) and 2-Propanol 99.5 % (Aldrich chemical Co, Inc). compound of PTFE, Activated Carbon and Alcohol called carbon Ink and fabrication result compound between carbon ink with carbon cloth called Gas Diffusion Layer (GDL) whereas GDL is embedded c with carbon ink catalyst called GDE. In this paper which evaluated is GDL whereas GDE will be there in the latter paper. Then to know GDL morphologi. GDL using SEM method, characterisation of surface area by metode BET. Knowing diffusivity by metode Ruthven (Ruthven ,1997, Do,1998) and to know MEA polarisation voltage and current by metodology of Programmer Fuel Cell Group (FCUKM,2002).

4.RESULT AND DISCUSSION

Surface area pore of Gas Diffusion Layer in our experiment, the fulfilled carbon to sprayer has $1650 \text{ m}^2/\text{g}$ surface area with 22 \AA pore diameter. After that the carbon ink with 1.5 cp viscosities will be fulfilled to sprayer that consists of 20 ml alcohol, 2.156 g activated carbon and PTFE from 0 to 10 % concentration. Another material that we used is 50 cm^2 wide carbon cloth. The sprayer has 60 cm/min x-axis spraying speed with static y-axis and height in z-axis of 12 cm. The draying temperature has to be set to 110°C for 4 hours processing time. From experiment, we could observe that with larger PTFE composition, the DGL pore diameter will decrease. Using DR method Autosorb-1 we found that with 2% to 5% PTFE composition has pore diameter of 4.5 to 9 \AA . In the DGL, the pore diameter is smaller than 20 \AA and larger than H_2 molecules 3.464 \AA (Michaelides, 1998). Based on Gregg's classifications (1982), the growth pore diameter is still above classified micropore.

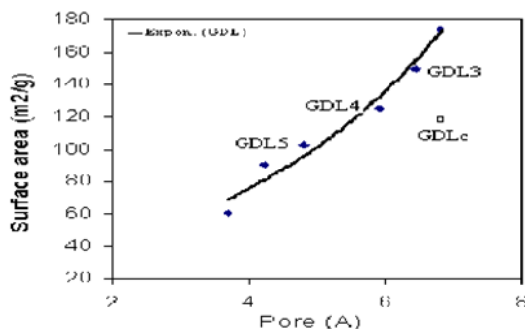


Fig.2. Effect pore on Surface Area

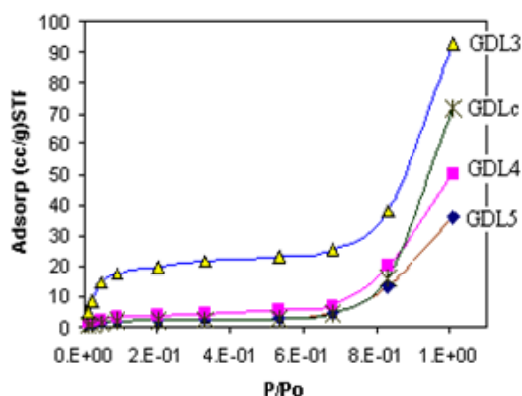
Table:1 Experimental data of Gas Diffusion Layer (GDL)				
PROPERTY ON MEA FUEL CELL	GDL5	GDL4	GDL3	GDE Commerce.
Operating pressure	1 bar	1 bar	1 bar	1 bar
Operating temperature	80 °C	80 °C	80 °C	80 °C
Cell voltage	0.65 V	0.65 V	0.65 V	0.65 V
Dissolved hydrogen con. At a reference	5.19 mol m ⁻³	5.19 mol m ⁻³	5.19 mol m ⁻³	5.19 mol m ⁻³
Dissolved oxygen con. at a reference	3.16 mol m ⁻³	3.16 mol m ⁻³	3.16 mol m ⁻³	3.16 mol m ⁻³
Potential in the electrode phase	1.0 V	1.0 V	1.0 V	1.0 V
Potential in the membrane phase	0.0 V	0.0 V	0.0 V	0.0 V
Potential different between electrode and Membrane at equilibrium	0.0 V	0.0 V	0.0 V	0.0 V
Active layer thickness of the electrode	466 μm	466 μm	466 μm	480 μm
Dry porosity of the anode electrode	0.1	0.1	0.1	0.1
Dry porosity of the cathode electrode	0.4	0.4	0.4	0.4
Faraday's constant	96487 A.s mol ⁻¹	96487 A.s mol ⁻¹	96487 A.s mol ⁻¹	96487 A.s mol ⁻¹
Diffusion coefficient of the dissolved hydrogen gas inside the micro porous	8.25x 10 ⁻⁶ m ² s ⁻¹	7.61x 10 ⁻⁶ m ² s ⁻¹	6.08x10 ⁻⁶ m ² s ⁻¹	8.76 x 10 ⁻⁶ m ² s ⁻¹
Micro porous radius	6.5 10 ⁻¹⁰ m	5.99x10 ⁻¹⁰ m	4.79x10 ⁻¹⁰ m	6.9x 10 ⁻¹⁰ m
Anode exchange current density	1x10 ³ A.m ⁻²	1x10 ³ A.m ⁻²	1x10 ³ A.m ⁻²	1x10 ³ A.m ⁻²
Cathode exchange current density	1.0 A.m ⁻²	1.0 A.m ⁻²	1.0 A.m ⁻²	1.0 A.m ⁻²
Specific surface area	1.59 10 ³ m ² m ⁻³	2.65 x10 ³ m ² m ⁻³	2.66 x10 ³ m ² m ⁻³	1.71 x 10 ³ m ² m ⁻³

Width of gas channel	0.0015 m	0.0015 m	0.0015 m	0.0015 m
Henry's constant for hydrogen	$3.9 \cdot 10^4 \text{ Pa m}^3 \text{ mol}^{-1}$	$3.9 \cdot 10^4 \text{ Pa m}^3 \text{ mol}^{-1}$	$3.9 \cdot 10^4 \text{ Pa m}^3 \text{ mol}^{-1}$	$3.9 \cdot 10^4 \text{ Pa m}^3 \text{ mol}^{-1}$
Henry's constant for oxygen	$3.2 \cdot 10^4 \text{ Pa m}^3 \text{ mol}^{-1}$	$3.2 \cdot 10^4 \text{ Pa m}^3 \text{ mol}^{-1}$	$3.2 \cdot 10^4 \text{ Pa m}^3 \text{ mol}^{-1}$	$3.2 \cdot 10^4 \text{ Pa m}^3 \text{ mol}^{-1}$

If GDL with 10.000 times enlargement. Each of the GDL ball shape particle consists of pore around 4.5 to 9 Å. With larger PTFE composition using sprayer method will grow larger such kind of particle (around 160 to 330 nm). It means that with larger PTFE composition, the micro pore will tend more dominant than the macro pore. From the mentioning above, we could conclude that GDL is a micro pore type as shown in Figure 3, and the larger pore diameter will be reached with larger pore surface area. The increasing of PTFE composition in GDL will decrease the surface area of active carbon particle that used in the sprayer.

From Figure 3, we could also conclude that our GDL (GDL3) has $151 \text{ m}^2/\text{g}$ active carbon surface areas. Our active carbon surface area is still above the commercial GDL with around $110 - 120 \text{ m}^2/\text{g}$ but below $200 \text{ m}^2/\text{g}$ that based on Ruthven means still has micro porous model property. And finally, we could conclude that surface area of GDL3 is suitable for Gas Diffusion Electrode (GDE) anode of MEA.

Fuel Cell Voltage /Current model. Figure 4 shows the Autosorb-1 method where the adsorption of nitrogen on GDL was carried out at 77 K and with the pressure ratio P/P_0 varies from 0 to 1.



Based on nitrogen physisorption on micro porous model in ml/g unit of calculation using DA method will be acquired 95 cc(STP)/g GDL3 maximum capacity of adsorption or still 24 cc (STP)/g above the commercial GDL or even 43 cc(STP)/g below G300 material (Dillen, 2001). Compared to commercial- and G300 GDL the GDL3 have better performance due to larger maximum capacity of adsorption and could be expanded as GDE anode of MEA. Therefore, in the implementation of GDL, hydrogen will diffuse from GDL interface to surface headed to catalyst. Using Ruthven equation (Ruthven 1997) for the diffusivity of hydrogen gas inside GDL structure at 70°C and 1 Atm pressure has been calculated within $8.25 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$ up to $6.08 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$, meanwhile GDLc about $8.76 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$. It has been reported that the range of diffusivity is still very impressive for mass and transport application (Lean 2002). We have observed that the diffusivity indicates the performance of GDL is correlates with Teflon distribution and porosity of GDL on carbon cloth.

In application fuel cell, the sum of gas for time accros from DGL to electrode area is made as surface area pore GDL (cm^2) is multiplied gas flux ($\text{gmol cm}^{-2} \text{ second}^{-1}$).

This gas will be reaktion at surface area pore carbon-platinum to produce electron and proton.

Then electron (current) accros GDL before enter cathode. From this, each of surface area micropore GDL will produce cell potential. Base on experiment and design data of simulation cell potential on table 1 will show profil of performance polarization fuel cell like figur 5.

In figure 5, each of Surface area GDL that are GDL5, GDL4, GDL3 and GDL Commerce having surface area $1.59 \times 10^3 \text{ m}^2\text{m}^{-3}$, $2.65 \times 10^3 \text{ m}^2\text{m}^{-3}$, $2.66 \times 10^3 \text{ m}^2\text{m}^{-3}$ and $1.71 \times 10^3 \text{ m}^2\text{m}^{-3}$.

GDL5, produce electric 0.63 A/cm^2 , GDL 4 of 0.86 A/cm^2 , GDL3 of 1 A/m^2 and GDLc is 0.65 A/m^2 . All of performance GDL experiment have the same profil with GDLc and current GDL3 has more than GDLc. From figure or data, can be conclude that surface area GDL is big more will get higher current fuel cell. This means surface area very influence performance current fuel cell. GDL have microporous properties model which have higher current than makro homegeneous dan aglomerate (Sui et al,1999) although GDL Voltage is lower. Used as parameter in GDL fabrication.

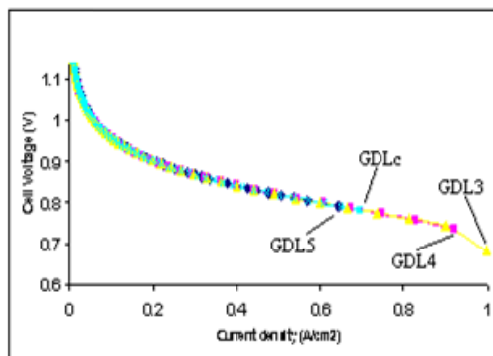


Fig 4. Fuel Cell voltage and Current model

5.CONCLUSION

The increasing of PTFE composition in GDL will decrease the surface area of active carbon particle which used in the sprayer. We could conclude that surface area of GDL3 include micro porous model property and GDL3 is suitable for Gas Diffusion Electrode (GDE) anode of MEA. Compared to commercial, the GDL3 have better performance due to larger maximum capacity of adsorption and could be expanded as GDE anode of MEA because of the range of diffusivity is still very impressive for mass and transport application. Surface area GDL is bigger then MEA Fuel Cell will produce higher current. Then, surface area GDL can be took as of the any parameter control to get performance MEA suitable to Fuel Cell.

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REFERENCES

- Gregg ,S.J. and Sing, K.S.W. 1982. Adsorption, Surface Area and Porosity. Academic Press london. New York Nijkamp, M.G, Raaymakers, J.E.M.J., Van
- Ruthven D. 1997. Encyclopedia of Separation Technology. Vol., John Wley, New York
- Do and K. Wang.1998. Dual Diffusion and Finite Mass Exchange Model for Adsorption Kinetics in Activated Carbon. AIChE Journal, 41, 68
- Xue-Dong Din and Efsthioosh , Emicchaelides, E.1998.Tansport Processes Of Water and Protons Through Micropores. AIChE Journal, 44, No1
- Marr, C. & Li, X. 1999. Composition and performance modelling of catalyst layer in a proton exchange membrane fuel cell. *Journal of Power Sources* 77: 17 – 27
- Sergei, G. 2002. Recent progress in performance improvement of the proton exchange membrane fuel cell (PEMFC). *Journal of Power Sources* 107: 5 – 12.



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- Ticianelli, E.A. Derouin, C.R. Redondo, A. & Srinivasan, S. 1988. Methods to advance technology of proton exchange membrane fuel cells. *J. Electrochem. Soc.* 135: 2209 – 2214
- Marr, C. & Li, X. 1999. Composition and performance modelling of catalyst layer in a proton exchange membrane fuel cell. *Journal of Power Sources* 77: 17 – 27
- Raimundo, R.P. & Ticianelli, E.A. 2002. Effect of the operation conditions on the membrane and electrode properties of a polymer electrolyte fuel cell. *J. Braz. Chem. Soc* Vol. 12, No. 4: 483 - 489.
- Lean, G., Djilali, N., Whale, M., Niet, T. 2000. Application of Micro-Scale Techniques to Fuel Cell Systems Design. Institut for Integrated Energy Systems, University of Victoria, B.C., Canada, VBW3P6
- Mar. X. Li. 1998. An Engineering model of Proton Exchange membrane Fuel Cell Performance. Ari 50:190-200, Springer-Verlag
- Sui and L.D. Chen. 1999. Modeling and Optimization of PEMFC Catalyst Layer. Honda RUD Cd. Ltd Jepun
- EG & G Service. 2000. Fuel Cell Handbook. Science Applications International Corporation. U.S. Department of Energy National Energy Technology Laboratory, Morgantown, West Virginia 26507-0880
- AG & G Services Person Inc. 2000. Fuel Cell Handbook. U.S. Department of Energy offices of Fossil Energy, Morgantown, West Virginia 26507- 0880
- Sharon Thomas and Zalbowitze. 1998. Fuel Cells-Green Power. Los Alamos National Laboratory, Los Alamos, New Mexico